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Theoretical Investigations of HEDM

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Introduction

The computational and theoretical chemistry group in the Propulsion Sciences Division at the Air Force Research Laboratory (AFRL) is engaged in several projects that support experimental research in the high energy density matter (HEDM) program. The spectral theory of chemical binding continues to be developed and implemented, providing a new framework for constructing adiabatic potential-energy surfaces for aggregates of interacting atomic or molecular species and giving insights into the structural and spectroscopic properties of HEDM-seeded cryogenic propellants. Preliminary applications to metal-doped rare gas matrices, such as sodium and aluminum atoms in argon, are invaluable to guiding theoretical understanding and computational implementation of the method. Secondly, calculations of structures and infrared spectra are assisting in the identification of new HEDM and other molecules produced by co-deposition of argon with the vapor from high-temperature evaporation of elemental powders, such as carbon and boron. Several new B_mC_n and C_n species ($m = 1-4$; $n = 2-13$) have been produced; the first identification of cyclic forms of small neutral polycarbons (C_6 and C_8) are notable accomplishments made possible by close interaction between theoreticians and experimentalists. Thirdly, the structures, spectra, and thermodynamic properties of proposed and synthesized new oxidizers, fuels, and monopropellants are also being calculated. An overview and highlights of these efforts are presented in this report, with further details on specific topics provided in other contributions to these proceedings [1-6].

Spectral Theory of Chemical Binding

A prominent goal of the HEDM program is to determine whether cryogenically solidified propellants (particularly H_2 or O_2) can be used as matrix materials in which significant quantities of atomic or small molecular additives can be trapped, thereby increasing the energy content of the propellant [7]. The spectral theory of chemical binding, which has been under development for about two years [8,9], aims to provide accurate electronic potential-energy surfaces for such aggregates, which in turn reveal their structural and spectroscopic properties, as well as information related to their stabilities and reactivities. Details of the theoretical approach are

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provided elsewhere in these proceedings [1,2], but its key features are as follows: (1) it treats physical and chemical binding on a common basis; (2) it gives a rigorous theoretical foundation for a class of methods, loosely known as "atoms-in-molecules" or "diatomics-in-molecules" approaches, which build potential surfaces from information related to component fragments [10-12]; (3) it requires only diatomic molecule calculations from conventional quantum chemistry, and these can be performed once and for all for any pair of atoms; and (4) it is potentially applicable to systems of 1000 or more atoms.

Due to the availability of experimental data on the spectroscopy of alkali atoms trapped in rare-gas matrices [13], these systems have been studied as prototypes of proposed HEDM fuels, such as atom-seeded solid H_2 . Potential-energy, dipole-moment, and transition-moment functions for the ground and lowest nine excited states of NaAr are calculated employing multireference configuration interaction (MRCI) from complete-active-space self-consistent-field (CASSCF) wave functions in large Gaussian atomic basis sets [14] supplemented with suitable diffuse functions. The NaAr potential-energy curves and selected dipole and transition moments so obtained are highlighted elsewhere in these proceedings [1]. Similar calculations for AlAr are in progress; preliminary results obtained employing MRCI from selected CASSCF configurations are shown in another abstract in this volume [2]. These data are used directly in computational implementations of the spectral theory and in ensuing simulations of the structures and absorption spectra of $NaAr_n$ and $AlAr_n$ clusters [1,2].

Identification of New Molecules

Another significant effort within the HEDM program at AFRL is the preparation and identification of new molecules that might prove to be suitable energetic additives to solidified propellants [7]. Additionally, it is essential to understand how HEDM additives deposited in cryogenic matrices might recombine to form larger systems, which requires identifying condensation products and mechanisms. In the course of experiments aimed at depositing a few mole percent carbon atoms in cryogenic matrices, a novel condensation chemistry has been observed with cyclic C_6 playing a leading role [15].

Pure carbon molecules (polycarbons) have received considerable experimental and theoretical attention over the past forty years. Several reasons were indicated by Weltner and Van Zee in their comprehensive review [16], including the possible role of polycarbons as soot precursors and their significance in astrophysical processes. More recently, the discovery of methods for producing macroscopic quantities of fullerenes in the laboratory [17,18] and the exploration of mechanisms for their formation have excited new interest. Vibrational and electronic spectra of linear C_6 have been extensively studied [19-29], but experimental data concerning possible cyclic forms are inconclusive. Several researchers have considered the question of why no cyclic forms of any small neutral polycarbons have been directly identified [23,30]; their elusiveness constitutes a long-standing experimental challenge.

The measurement and assignment of cyclic C_6 in argon matrices is discussed elsewhere in these proceedings [4]; here the focus is on the details of the calculations. Previous studies of C_6 isomers employing extensive electron-correlation treatments [30-34], including single- and double-excitation coupled-cluster calculations with a noniterative treatment of connected triple

excitations [denoted CCSD(T)], indicate that the distorted hexagon (${}^1A_1'$, D_{3h} symmetry) is ~ 8 kcal/mol lower in energy than the regular hexagon (${}^1A_{1g}$, D_{6h}) and ~ 11 kcal/mol lower than the linear chain (${}^3\Sigma_g^-$, $D_{\infty h}$). Additionally, application of density-functional theory (DFT) methods to cyclic C_6 [35,36] yields structures, frequencies, and intensities that are in good accord with the CCSD(T) results [30,34]. Whereas harmonic frequencies and infrared intensities for cyclic ${}^{12}C_6$ have been published [33-37], the ${}^{13}C$ isotopic shifts essential for the definitive identification of matrix-isolated species are not in the literature. Consequently, density-functional (B3LYP) calculations in several atomic basis sets were performed, as were CCSD(T) calculations in the cc-pVDZ basis set, largely following the work of Martin and co-workers [34,36].

Vibrational frequencies and intensities were computed for the complete set of isotopomers; those for the vibrational modes of cyclic ${}^{12}C_6$ are reported in Table 1. These data are evidently insensitive to the choice of atomic basis set or correlation treatment, and the B3LYP/cc-pVDZ results are in complete agreement with those from the identical calculation of Martin *et al.* [36]. Our CCSD(T)/cc-pVDZ frequencies (Table 1), however, differ significantly from those reported by Martin and Taylor [34], even though we obtained the same minimum energy structure is obtained. These results were confirmed using two different program systems [38,39], strongly indicating that the CCSD(T)/cc-pVDZ frequencies for cyclic ${}^{12}C_6$ reported by Martin and Taylor (Table 3 of Ref. 34) should be replaced by the values listed in Table 1. The scale factor for the $\nu_4(e')$ mode that brings the calculated CCSD(T)/cc-pVDZ frequency into coincidence with the measurement is 0.9762, sufficiently near unity to tentatively assign the 1694.7 cm^{-1} band to cyclic ${}^{12}C_6$. Conclusive assignment, however, is based on the ${}^{13}C$ isotopomer data, which is also in excellent accord with experimental observations [4]. Similar studies of cyclic C_8 and several mixed boron/carbon clusters are in progress.

Properties of New Propellant Ingredients

A third prominent area of research within the HEDM program is the synthesis and characterization of new fuels, oxidizers, and monopropellants to supplement or replace current propellants. Calculations support synthesis efforts by providing accurate structural parameters and thermodynamic data, as well as infrared, Raman, and nuclear magnetic resonance spectra. Additionally, potential-energy surfaces may be examined to determine transition states and barriers to decomposition. Several calculations related to current chemical synthesis at AFRL are reported in other abstracts in these proceedings [3,5,6]; compounds examined include molecules such as nitrocyanamide anion [6], triazidocarbenium cation [5], and spiro-bis-oxetane [4]. In general, these studies involve computing structures, spectra, and heats of formation employing Hartree-Fock, density-functional, and coupled-cluster methods in double- or triple-zeta atomic basis sets. For nitrocyanamide anion and its protonated form, heats of formation of -2 and $+55$ kcal/mol were found by the Gaussian-2 ("G2") method [6], which compare with the value of -29 kcal/mol calculate for dinitramide anion $[(NO_2)_2N]^-$. The heat of formation of spiro-bis-oxetane, calculated at the MP2/6-31G(d)//HF/6-31G(d) level, is -28 kcal/mol [4]. Data such as this is useful in determining whether proposed or synthesized molecules are suitable candidate ingredients for energetic propellants.

Conclusion

The computational and theoretical chemistry group at AFRL is supporting a wide variety of experimental research within the HEDM program; Table 2 gives a summary of these efforts. The methods employed range from the development of new theories and associated computer programs to the application of well-known techniques and codes to problems in energetic material synthesis and characterization. The impact of these calculations included screening of candidate synthesis targets and identification of unknown molecules, along with predictions of their properties and stabilities. It is clear that *ab initio* quantum chemistry contributes to one of the missions of AFRL -- to create technologies for the war fighter to control and exploit space -- by pointing the way to new chemical propellants with increased performance characteristics.

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Table 1. Calculated harmonic frequencies (cm^{-1}) of cyclic $^{12}\text{C}_6$. Infrared intensities (km/mol) of the active modes are given in parentheses.

Mode	B3LYP/6-311G(2d)	B3LYP/cc-pVDZ	B3LYP/cc-pVTZ	CCSD(T)/cc-pVDZ
$\nu_1(a_1')$	1218	1222	1223	1183
$\nu_2(a_1')$	646	659	647	556
$\nu_3(a_2')$	1393	1437	1412	1371
$\nu_4(e')$	1751 (424)	1769 (404)	1761 (436)	1736 (420)
$\nu_5(e')$	1234 (1)	1219 (1)	1232 (1)	1178(1)
$\nu_6(e')$	650 (24)	633 (25)	645 (22)	576 (43)
$\nu_7(a_2'')$	425 (7)	419 (8)	435 (6)	380 (7)
$\nu_8(e'')$	534	519	538	492

Table 2. Summary of HEDM-related computations at AFRL.

Area of Interest	Type of Calculation	Impact of Calculations	Applications
Synthesis of new propellant ingredients	Calculations of stationary points on potential surfaces	Exploration of efficient synthetic routes and dissociation pathways	Cubane (C_8H_8), pentaprismane ($\text{C}_{10}\text{H}_{10}$)
Stabilities of proposed and synthesized new propellants	Calculations of structures, spectra, properties	Effective screening of proposed compounds; determine which merit experimental study	$[(\text{N}_3)\text{C}]^+$, $[\text{NCNNO}_2]^-$, $\text{C}_5\text{H}_8\text{O}_2$, $\text{C}_{17}\text{H}_{24}\text{N}_4\text{O}_8$
Discovery and characterization of new cryogenic HEDM additives	Calculations of infrared frequencies and intensities; spectral modeling	Predict whether candidate molecules can be isolated; aid in data analysis	Li_xB_y , Li_xC_y , Si_xC_y ($x, y = 1, 2, 3$); cyclic C_6 and C_8
Characterization of doped cryogenic solid propellants	Spectral theory of chemical binding in conjunction with molecular dynamics simulations	Predict structures, densities, dopant concentrations, and stabilities of cryogenic HEDM propellants	Na/Ar_n , Al/Ar_n (prototypes); Li/H_2 , B/H_2 , LiB/H_2 , $\text{B}/\text{H}_2/\text{He}_{(l)}$